Computer simulation of decay kinetics of solitons and polarons in linear chain lattices

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Abstract

The diffusion-limited collisional decay process of solitons and polarons excited in a linear chain lattice is simulated numerically. The dependence of the survival function on the initial density and lattice disorder is examined. In the uniform chain, if the initial density N_0 is sufficiently low, the probability of solitons surviving at a time t agrees well with Torney and McConnell's solution $S(\zeta)=\exp(8\zeta)\mathrm{erfc}(8\zeta)^{1/2}$, $\zeta=N_0^2Dt$, for the unimolecular chemical reaction in a continuous medium, where D is the diffusion constant; the lattice effect appears with increasing N_0 as the slowing down of the initial decay. The survival probability of polarons is also given by a universal function $S(\zeta)=(1+33\zeta)^{-1/4}$ within errors of ±2%. As the lattice disorder evolves, $S(\zeta)$ transforms into the Kohlrausch law $S(\zeta)=\exp\{-(\zeta/\zeta_0)^{\beta}\}$, $0<\beta<1$, for both solitons and polarons, consistent with the experiment for long-lived photoexcited solitons in an MX chain compound.

key words : computer simulations, photoexcitations, decay kinetics, linear chain lattices

1. Introduction

Photoexcited solitons [1] and polarons [2] in conducting polymers show an extremely nonexponential time decay. According to the recent decay measurement of the photoinduced midgap absorption in an MX chain compound [3], the density $N(t)$ of long-lived solitons obeys the -log$t$ law or the Kohlrausch law

$$S(t) \equiv N(t)/N_0 = \exp\{-(t/\tau)^{\beta}\} \quad \text{with } 0<\beta<1\,, \qquad (1)$$

where N_0 is the initail density of photoexcited solitons, t is the time delay and τ is the $1/e$ decay time. The experiment shows that τ depends strongly on temperature, whereas β is a constant of 0.27 – 0.54 depending on samples. These facts suggest that the solitons walk randomly in the MX chain by hopping over irregular energy barriers until they collide with antisolitons to coalesce.

To understand these novel dynamical properties we perform a numerical simulation of the diffusion-limited pair coalescence of solitons and polarons in disordered one-dimensional lattices.

2. Results and Discussion

The calculation is carried out by the standard method. We deal with a chain ring of 10,000 lattice sites. Initially, 500 to 5,000 particles are placed randomly in the ring on the basis of the binomial, unimolecular and bimolecular occupation for solitons and polarons, respectively. Then we let the particles hop randomly to adjacent sites. The probability of hopping from the site i to the adjacent site j=i+1 is assumed to be given by $\nu=\nu_0\exp(-E_{ij}/kT)$ at temperature T, where ν_0 is set to be 10^6/step and the energy barrier

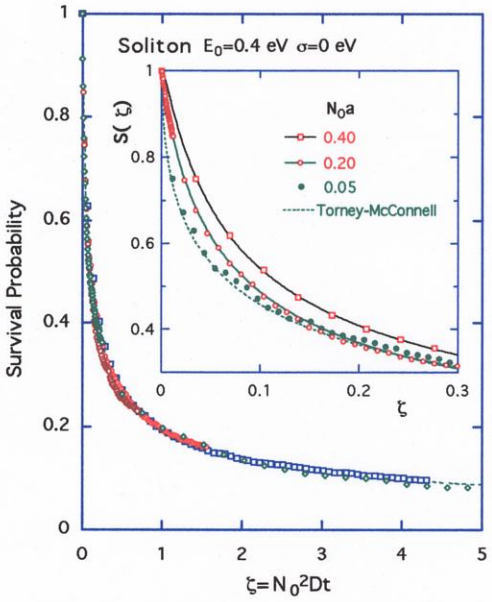

Fig. 1. Survival probability $S(\zeta)$ of solitons in the uniform chain. The markers are the calculated values and the dotted line shows $S^{TM}(\zeta)$. The inset shows $S(\zeta)$ and $S^{TM}(\zeta)$ for $0\le\zeta\le0.3$.

E_{ij} is assumed to be fluctuated randomly around the mean value E_0 with a Gaussian width σ. We deal with the range of T between 200 and 300 K by fixing E_0 at 0.4 eV and permitting σ to vary from 0 to 0.1 eV. This choice of the value for E_0 does not lose the generality, because the physical conditions of the medium are specified by the

ratios E_0/kT and σ/E_0. Once two solitons or oppositely charged two polarons come on the same lattice site, they are removed. Interactions between particles are ignored in the present study.

To begin with, we calculate S(t) for solitons in the uniform lattice ring (σ=0) under various conditions of the initial density and temperature. Figure 1 shows the plot of the results, in which $\zeta = N_0^2Dt$ with $D = a^2\nu_0\exp(-E_0/kT)$ is taken as the variable, where a denotes the lattice constant. Torney and McConnell's survival function, $S^{TM}(\zeta) = \exp(8\zeta)\mathrm{erfc}(8\zeta)^{1/2}$ [4], erfc denoting the complementary error function, is also drawn along with the calculated values. $S^{TM}(\zeta)$ is the solution for the unimolecular chemical reaction in a continuous ring. It gives S(ζ) of solitons in the limiting case of $N_0a \to 0$ of our lattice ring model. Consequently, although the result of our calculation agrees well with $S^{TM}(\zeta)$ in a wide range of ζ, there is a significant disagreement in the initial part. As N_0a approaches zero, this lattice effect tends to be smeared, and thus S(ζ) approaches $S^{TM}(\zeta)$ asymptotically.

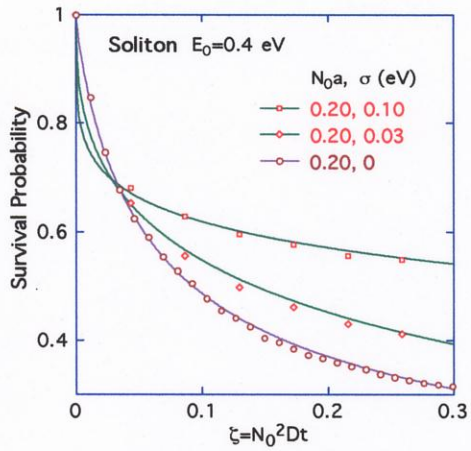

Fig. 2. Variation of S(ζ) of solitons with σ.

S(ζ) is nonexponential, reflecting the nonlinearity of the geminate coalescence. It becomes still more nonexponential if the energy barriers are irregular. Figure 2 shows the results of calculation for the case of $N_0a = 0.2$. We see that as σ increases, S(ζ) transforms into the Kohlrausch law, $S(\zeta) = \exp\{-(\zeta/\zeta_0)^{\beta}\}$, as expected. The Kohlrausch law holds in the variation of ζ over more than several orders, as shown in Fig. 3. The argument β decreases from ~0.5 to 0.25 with increasing σ from small values to 0.1 eV(=0.25E_0). This fact explains the aforementioned sample dependence of β well. Also the decay parameter ζ_0 depends on σ. As far as $N_0a < 0.1$, the lattice effect is sufficiently small that τ varies with N_0 and D as $N_0^{-2}D^{-1}$ with the coefficient ζ_0. It is noteworthy that the decay time τ is not a material constant.

Figure 4 shows S(ζ) of polarons in the case of σ=0. We find that S(ζ) is given by a universal function of ζ also in this bimolecular recombination process. If $N_0a < 0.2$, S(ζ) can be expressed well in terms of an empirical formula $S(\zeta) = (1+33\zeta)^{-1/4}$, the error being smaller than ±2% for any value of ζ. As N_0a increases beyond 0.2, the initial part of S(ζ) deviates upward because of the lattice effect. For $\zeta > 1$, since the self assembling

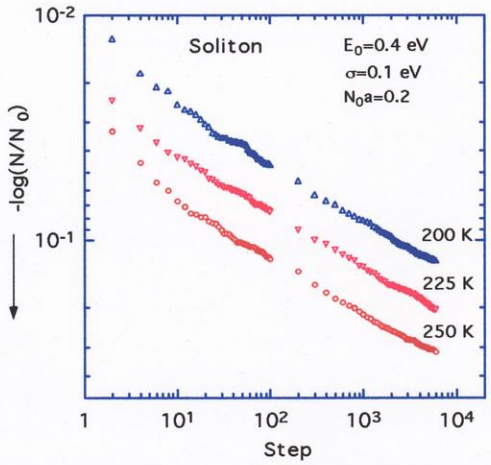

Fig. 3. Log(-logS(t)) versus log$t$ for the case of σ=0.25E_0 at different temperatures.

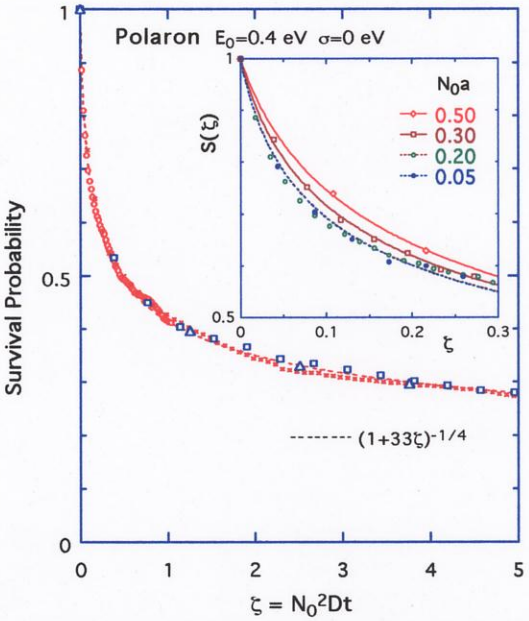

Fig. 4. S(ζ) of polarons in the uniform chain. The markers are the calculated values and the dotted line shows the curve of $(1+33\zeta)^{-1/4}$. The solid lines are the guides for the eye.

properties of polarons function to slow down their decay [5], S(ζ) varies as $\zeta^{-1/4}$, in contrast to the $\zeta^{-1/2}$ variation of S(ζ) of solitons for $\sigma = 0$. If σ exceeds 0.025E_0, the influence of the irregularity of the energy barriers becomes significant, leading S(ζ) to obey the Kohlrausch law, as observed in polymers [2].

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